# Alkynylethers en -thioethers

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## SUMMARY

*Chapter I* deals with the preparation of 1-alkynylethers ($RC{\equiv}CCR'$). A number of these compounds (table I, page 12) was synthesized, making use of the so called "classical method", which is shown in the following scheme:

$$RCH_2CHO + R'OH \xrightarrow{HCl} RCH_2CHCl(OR') \xrightarrow{Br_2} RCHBrCHBrOR' \xrightarrow{C_6H_5N(C_2H_5)_2} RCBr{=}CHOR' \xrightarrow[\text{or better } NaNH_2]{KOH} RC{\equiv}COR' \quad (1)$$

cis + trans

With the exception of $R'{=}C(CH_3)_3$, R and R' in compounds of type $RC{\equiv}COR'$ may be a normal or branched alkyl group.

The use of sodamide in liquid ammonia in the last step is very advantageous. The ethers obtained by means of sodamide are listed in table II page 13. If $R{=}CH_3$, an excess of sodamide may cause isomerisation to 3-propynylethers (II):

$$\underset{\text{I}}{CH_3C{\equiv}COR'} \overset{NaNH_2}{\rightleftharpoons} CH_2{=}C{=}CHOR' \overset{NaNH_2}{\rightleftharpoons} \underset{\text{II}}{HC{\equiv}CCH_2OR'} \quad (2)$$

A simpler method for the synthesis of alkynyl ethers makes use of alkylation of sodium- or lithium alkoxyethynylide in liquid ammonia (table IV, page 18).

$$\left.\begin{matrix}Li\\Na\end{matrix}\right\} C{\equiv}COR' + RX \xrightarrow{NH_3} RC{\equiv}COR' + \left\{\begin{matrix}Li\\Na\end{matrix}\right\} X \quad (3)$$

Sodium alkoxyethynylide can be obtained from chloro acetal, from *cis* or *trans* alkyl β-halovinyl ether, or from alkoxyethyne, with sodamide; the lithium compound from *cis* or *trans* alkyl β-halovinyl ether or alkoxyethyne, and lithium amide.

The alkylation can be performed only with primary alkyl halides.

Using this method some *tert.* butyl ethers $RC{\equiv}COC(CH_3)_3$ were prepared.

α, ω-Dihalides can also be used, yielding compounds of type $ROC{\equiv}C(CH_2)_n C{\equiv}COR$.

*Chapter II* is devoted to the preparation of ethers of type $RC{\equiv}C\text{-}OCH_2CH_2O\text{-}C{\equiv}CR$. These are accessible by application of the "classical method" as well as by alkylation.

In *chapter III* a method is described for the introduction of alkylthio groups into compounds with reactive hydrogen atoms. This method consists of treatment of the appropriate carbanions with dialkyl disulphides in liquid ammonia. The major

product in the case of acetone, *tert.*. butyl acetate and diphenylmethane is the result of substitution of two of the geminal hydrogen atoms by alkylthio groups:

$$CH_3COCH_3 \xrightarrow[RSSR]{LiNH_2} CH_3COCH_2SR \xrightarrow[RSSR]{LiNH_2} CH_3COCH(SR)_2 \qquad (4)$$

Malonic ester did not react under these circumstances.

Application of this "alkylthiolation" to alkynes, led to a simple conversion of ethyne into 1-alkynylthioethers (RC≡CSR').

$$LiC{\equiv}CH \xrightarrow[NH_3]{RX} RC{\equiv}CH \xrightarrow[R'SSR']{LiNH_2} RC{\equiv}CSR' + LiSR' \qquad (5)$$

The reaction of diethyl disulphide with lithium chloroethynylide did not produce the expected product III, but rather 1,2-bis(ethylthio)ethyne (IV):

$$ClCH{=}CHCl \xrightarrow[NH_3]{LiNH_2} ClC{\equiv}CLi \xrightarrow[C_2H_5SSC_2H_5]{LiNH_2} ClC{\equiv}CSC_2H_5 + LiSC_2H_5 \longrightarrow \qquad (6)$$

III

$$(C_2H_5S)ClC{=}CH(SC_2H_5) \longrightarrow C_2H_5SC{\equiv}CSC_2H_5$$

IV

This is an excellent method for preparing 1,2-bis(alkylthio)-ethynes.

Similarly the reaction of diethyl disulphide with lithium ethoxyethynylide did not lead to V but to VI.

$$C_2H_5OC{\equiv}CLi + C_2H_5SSC_2H_5 \xrightarrow{NH_3} C_2H_5OC{\equiv}CSC_2H_5 + LiSC_2H_5 \longrightarrow \qquad (7)$$

V

$$(C_2H_5S)C_2H_5OC{=}CH(SC_2H_5)$$

VI

In *chapter IV* the preparation of compounds III en V, using thiolsulfonates ($RSO_2SR$) instead of dialkyl disulphides, is discussed.

$$XC{\equiv}CLi + RSO_2SR \longrightarrow XC{\equiv}CSR + RSO_2Li \qquad (X{=}OR, Cl) \qquad (8)$$

Compound V appeared to be very unstable, and could not be obtained in a pure state. Its existence, however, was proved by some addition reactions.

The compound III was also obtained by dehydrochlorination of 1,2-dichloro-1-(ethylthio)ethyne (equation 9) and by chlorination of ethylthioethyne with potassium hypochlorite (equation 10):

$$CHCl{=}CCl(SC_2H_5) + LiNH_2 \xrightarrow{NH_3} ClC{\equiv}CSC_2H_5 + LiCl + NH_3 \qquad (9)$$

$$HC{\equiv}CSC_2H_5 + KOCl \xrightarrow{2N\ KOH} ClC{\equiv}CSC_2H_5 + KOH \qquad (10)$$